

Quarterly Technical Report

Selected Energy Epitaxial Deposition and Low Energy
Electron Microscopy of AlN, GaN and SiC Thin Films

DISTRIBUTION STATEMENT A

Approved for public release
Distribution Unlimited

Supported under Grant #N00014-95-1-0122
Office of the Chief of Naval Research
Report for the period 4/1/97-6/30/97

DTIC QUALITY INSPECTED

R. F. Davis, H. H. Lamb[†] and I. S. T. Tsong*,
E. Bauer*, E. Chen[†], R. B. Doak*, J. L. Edwards*,
N. Freed*, J. Fritsch*, D. C. Jordan*, A. Michel[†], M. Meloni*,
A. Pavlovska*, K. E. Schmidt*, and V. Torres*

Materials Science and Engineering Department

[†]Chemical Engineering

North Carolina State University

Campus Box 7907

Raleigh, NC 27695-7907

and

*Department of Physics and Astronomy

Arizona State University

Tempe, AZ 85287-1504

June, 1997

19970821 123

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June, 1997	3. REPORT TYPE AND DATES COVERED Quarterly Technical 4/1/97-6/30/97	
4. TITLE AND SUBTITLE Selected Energy Epitaxial Deposition and Low Energy Electron Microscopy of AlN, GaN, and SiC Thin Films			5. FUNDING NUMBERS 1213801---01 312 N00179 N66020 4B855	
6. AUTHOR(S) R. F. Davis, H. H. Lamb and I. S. T. Tsong				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) North Carolina State University Hillsborough Street Raleigh, NC 27695			8. PERFORMING ORGANIZATION REPORT NUMBER N00014-95-1-0122	
9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES) Sponsoring: ONR, Code 312, 800 N. Quincy, Arlington, VA 22217-5660 Monitoring: Administrative Contracting Officer, Regional Office Atlanta Atlanta Regional Office 100 Alabama Street, Suite 4R15 Atlanta, GA 30303			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Tight-binding <i>ab initio</i> molecular-dynamics simulations involving a generalized multicenter tight-binding formalism which includes self-consistent charge transfer between the ions were used to investigate initial stages of growth of Group III nitrides. Initial results for the lattice constants, bulk modulus, phonon frequencies and electronic structure of the zincblende and wurtzite phase of bulk GaN and AlN are in good agreement with existing experimental data and highly converged plane-wave calculations. The calculated relaxation parameters and formation energies determined for stoichiometric and nonstoichiometric geometries agree very well with density-functional calculations. Vacancy structures are the most stable configurations on the anion and cation terminated surfaces. The effectiveness of a supersonic seeded-beam jet and an RF plasma, connected independently to a low energy electron microscope (LEEM), were compared as sources of nitrogen for the growth of gallium nitride films on 6H-SiC(0001) substrates. Growth of GaN films on chemically vapor deposited GaN/AlN/SiC substrates was accomplished using triethylgallium and NH ₃ -seeded supersonic molecular beams. The films were characterized by XPS, RHEED, SEM and AFM, and the effects of substrate temperature, NH ₃ flux and Ga flux on growth rate and film morphology examined. Typical GaN films grown at 700°C under NH ₃ -limited conditions exhibited a rough, highly faceted surface morphology; smoother surfaces are obtained when the Ga flux was increased. Nitridation experiments on Si(100) wafers were conducted using monoenergetic and mass separated ion beams of N ₂ ⁺ and N ⁺ produced in colutron ion sources. SIMS studies of the surfaces nitrided with both ions reveal slowly decaying nitrogen signals due to formation of SiN layers. Research is underway to deposit GaN layers by Ga ⁺ and N ₂ ⁺ (or N ⁺) beams.				
14. SUBJECT TERMS III-Nitrides, gallium nitride, GaN, aluminum nitride, AlN, molecular-dynamics, lattice constant, bulk modulus, phonon frequencies, electronic structure, vacancy structures, supersonic seeded-beam, RF plasma, low energy electron microscope, LEEM, homoepitaxial growth, XPS, RHEED, SEM, AFM, nitridation, Colutron and SIMS			15. NUMBER OF PAGES 25	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLAS	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLAS	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLAS	20. LIMITATION OF ABSTRACT SAR	

Table of Contents

I.	Introduction	1
II.	<i>Ab initio</i> Calculation of the Structure and Growth Properties of the III-V Nitrides	4
III.	<i>In situ</i> LEEM/LEED Studies of the Growth of GaN Layers on 6H-SiC(0001) Substrates using a Supersonic Seeded-Beam Jet Source	6
IV.	Selected Energy Epitaxial Deposition (SEED) of III-V Nitride and SiC Thin Films	14
V.	Dual Colutron Ion-Beam Deposition	23
VI.	Distribution List	25

I. Introduction

The realized and potential electronic applications of AlN, GaN and SiC are well known. Moreover, a continuous range of solid solutions and pseudomorphic heterostructures of controlled periodicities and tunable bandgaps from 2.3 eV (3C-SiC) to 6.3 eV (AlN) have been produced at North Carolina State University (NCSU) and elsewhere in the GaN-AlN and AlN-SiC systems. The wide bandgaps of these materials and their strong atomic bonding have allowed the fabrication of high-power, high-frequency and high-temperature devices. However, the high vapor pressures of N and Si in the nitrides and SiC, respectively, force the use of low deposition temperatures with resultant inefficient chemisorption and reduced surface diffusion rates. The use of these low temperatures also increases the probability of the uncontrolled introduction of impurities as well as point, line and planar defects which are likely to be electrically active. An effective method must be found to routinely produce intrinsic epitaxial films of AlN, GaN and SiC having low defect densities.

Recently, Ceyer [1, 2] has demonstrated that the barrier to dissociative chemisorption of a reactant upon collision with a surface can be overcome by the translational energy of the incident molecule. Ceyer's explanation for this process is based upon a potential energy diagram (Fig. 1) similar to that given by classical transition-state theory (or activated-complex theory) in chemical kinetics. The dotted and dashed lines in Fig. 1 show, respectively, the potential wells for molecular physisorption and dissociative chemisorption onto the surface. In general, there will be an energy barrier to overcome for the atoms of the physisorbed molecule to dissociate and chemically bond to the surface. Depending upon the equilibrium positions and well depths of the physisorbed and chemisorbed states, the energy of the transition state E^* can be less than zero or greater than zero. In the former case, the reaction proceeds spontaneously. In the latter case, the molecule will never proceed from the physisorbed state (the precursor state) to the chemisorbed state unless an additional source of energy can be drawn upon to surmount the barrier. This energy can only come from either (1) the thermal energy of the surface, (2) stored internal energy (rotational and vibrational) of the molecule, or (3) the incident translational kinetic energy of the molecule. Conversion of translational kinetic energy into the required potential energy is the most efficient of these processes. Moreover, by adjusting the kinetic energy, E_i , of the incoming molecule, it is possible to turn off the reaction ($E_i < E^*$), to tailor the reaction to just proceed ($E_i = E^*$), or to set the amount of excess energy to be released ($E_i > E^*$). The thrust of the present research is to employ these attributes of the beam translational energy to tune the reaction chemistry for wide bandgap semiconductor epitaxial growth.

The transition state, E^* , is essentially the activation energy for dissociation and chemisorption of the incident molecules. Its exact magnitude is unknown, but is most certainly

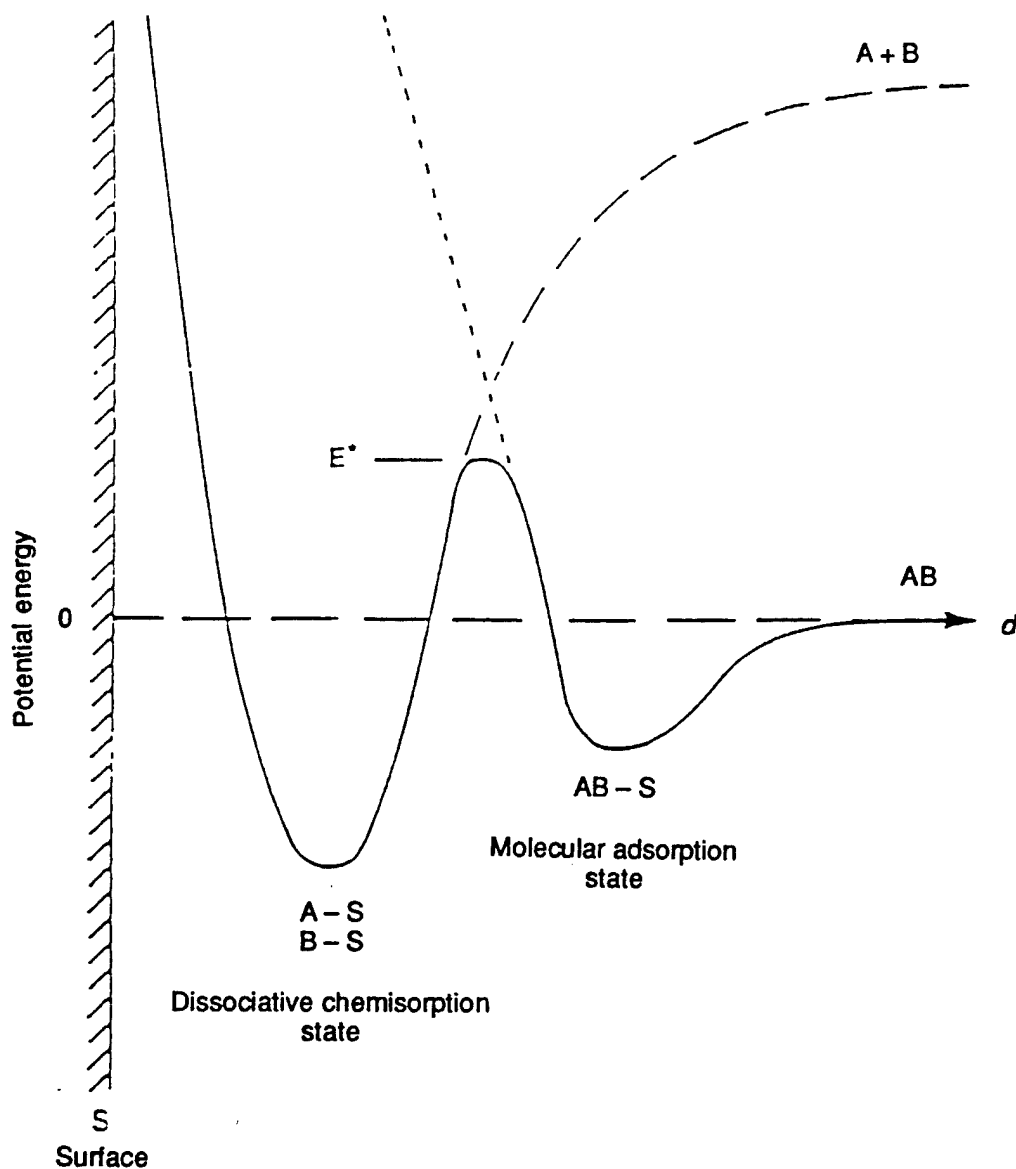


Figure 1. Schematic potential energy diagram of an activated surface reaction involving a molecularly physisorbed precursor state [from Ref. 1].

lower than the dissociation energy of the free molecule. It does not necessarily follow, however, that any kinetic energy above E^* will promote high-quality epitaxial growth of GaN. One must take into consideration another energy threshold, E_d , beyond which the kinetic energy of the incident flux will cause damage to the epitaxial film being synthesized. A typical E_d threshold value is approximately five times the bandgap of the crystal and in the case of GaN, $E_d \approx 18$ eV.

From the above consideration, it is clear that the key to high quality epitaxial growth is to be able to tune the energy of the incoming flux species over a range of energies defined by the window between E^* and E_d . Since the window is quite restrictive, i.e. 1-20 eV, it is essential that the energy spread of the flux species must be small, i.e. the flux species should ideally be

monoenergetic. To this end, we employ Selected Energy Epitaxial Deposition (SEED) systems for the growth of AlN, GaN and SiC wide bandgap semiconductors. The SEED systems are of two types: (1) a seeded-beam supersonic free-jet (SSJ) and (2) a dual ion-beam Colutron. Both these SEED systems have the desirable property of a narrow energy spread of ≤ 1 eV.

Epitaxial growth using the seeded-beam SSJ involves a close collaboration between investigators at NCSU and Arizona State University (ASU). At ASU, the SSJ is interfaced directly into a low-energy electron microscope (LEEM) for the conduct of *in situ* studies of the nucleation and growth of epitaxial layers; while at NCSU, the SSJ systems are used to grow device-quality AlN, GaN and SiC for real applications. Exchanges in personnel (students) and information between the two groups ensures the achievement of desired results. The additional thin film growth experiments using dual-beam Colutrons and the theoretical studies referred to in this report are primarily conducted at ASU.

The research conducted in this reporting period and described in the following sections has been concerned with (1) tight-binding *ab initio* molecular-dynamics simulations to investigate initial stages of growth of group III nitrides, (2) a comparison of the effectiveness of a supersonic seeded-beam jet and an RF plasma, connected independently to a low energy electron microscope, as sources of N for the growth of GaN films on 6H-SiC(0001) substrates, (3) growth and characterization via TEM and XPS of GaN films on chemically vapor deposited GaN/AlN/SiC substrates using triethylgallium and NH₃-seeded supersonic molecular beams, and (4) nitridation experiments on Si(100) wafers using monoenergetic and mass separated ion beams of N₂⁺ and N⁺ produced in Colutron ion sources. The following individual sections detail the procedures, results, discussions of these results, conclusions and plans for future research. Each subsection is self-contained with its own figures, tables and references.

1. S. T. Ceyer, Langmuir 6, 82 (1990).
2. S. T. Ceyer, Science 249, 133 (1990).

II. *Ab Initio* Calculation of the Structure and the Growth Properties of the Group III Nitrides

Tight-binding like *ab initio* molecular-dynamics simulations [1] is being used to investigate initial stages of the growth process of Group III nitrides films. Because of the ionicity of the Group III nitrides, the calculations have to be carried out on the basis of the generalized multicenter tight-binding formalism introduced by Demkov and co-workers [2] which includes charge transfer between the ions in a self-consistent fashion.

Initial studies concentrated on the determination of the lattice constants, bulk modulus phonon frequencies and electronic structure of the zincblende and wurtzite phase of bulk GaN and AlN. The results are in good agreement with existing experimental data and highly converged plane-wave calculations [3, 4, 5]. The computations have been expanded to the investigation of the surface atomic and electronic structure of the nonpolar (1010) and (1120) surfaces of GaN and AlN. The calculated relaxation parameters and formation energies determined for stoichiometric and nonstoichiometric geometries agree very well with the density-functional calculations of Refs. [6, 7].

A first important step for the investigation of the growth of wurtzite-phase GaN and AlN is to study the structural details of the uppermost layers of the growing film. The polarity of the ionic compounds substantially influences the atomic geometry of the hexagonal surfaces. Atomically flat surfaces are found to be highly unstable with respect to the formation of defect structures such as vacancies or adatom configurations. Vacancy structures are found to be the most stable configurations on the anion and cation terminated surfaces. For metal rich growth conditions, the calculations favor the adsorption of metal atoms on the cation terminated surface while the adsorption of hydrogen stabilizes flat surfaces in the presence of hydrogen. Decomposition of ammonia and subsequent adsorption of nitrogen and hydrogen is found to be exothermic.

The next step will consist of performing detailed investigations on the chemical reactions of ammonia on the cation and anion terminated surfaces of AlN and GaN. By means of *ab initio* molecular-dynamics simulations reaction paths can be determined for the impact of an ammonia molecule on the surface. It is planned to locate preferential adsorption sites and to study the relation between the surface morphology and/or stoichiometry and sticking probabilities. Various scenarios and configurations have to be considered. With the computation of potential energy surfaces for such adsorption processes, diffusion barriers can be determined. The calculated energies can serve as realistic input parameters for Monte Carlo simulations for large scale growth patterns in order to analyze the kinetic growth and nucleation mechanisms.

References

1. O. F. Sankey and D. J. Niklewski, Phys. Rev. B **40**, 3979 (1989).
2. A. A. Demkov, J. Ortega, O. F. Sankey, and M. Grumbach, Phys. Rev. B **52**, 1618 (1995).
3. A. F. Wright and J. S. Nelson, Phys. Rev. B **50**, 2159 (1994).
4. I. Gorczyka, N.E. Christensen, E.L. Peltzer y Blancá, and C.O. Rodriguez, Phys. Rev. B **51**, 11936 (1995).
5. K. Miwa and A. Fukumoto, Phys. Rev. B **48**, 7897 (1993).
6. J. E. Northrup and J. Neugebauer, Phys. Rev. B **53**, R10477 (1996).
7. K. Kádas, S. Alvarez, E. Ruiz, and P. Alemany, Phys. Rev. B **53**, 4933 (1996).

Publication

J. Fritsch, O. F. Sankey, K. E. Schmidt and J. B. Page, “*Ab initio* calculation of the stoichiometry and structure of the (0001) surfaces of GaN and AlN” Phys. Rev. B (submitted).

III. *In situ* LEEM/LEED Studies of the Growth of GaN Layers on 6H-SiC(0001) Substrates using a Supersonic Seeded-Beam Jet Source

A. Introduction

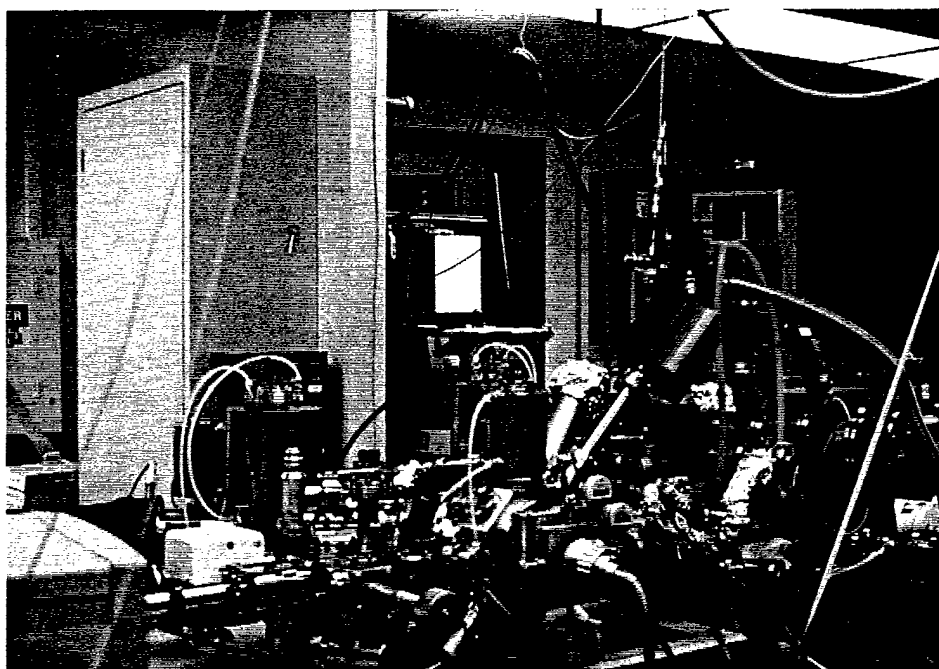
The previous report showed LEEM images and LEED patterns of GaN growth on a 6H-SiC(0001) substrate with an N-atom RF plasma source. The process started with nucleation at the step edges followed by growth of faceted crystals across the terraces. In the present report period, *in situ* GaN growth experiments were conducted in the LEEM with the supersonic nozzle or the supersonic seeded-beam jet (SSJ) source and the results were compared with those obtained with the RF plasma source. Additionally, in order to understand the influence of the substrate on the growth process, we undertook an in-depth study of the 6H-SiC(0001) surface prepared by etching with hydrogen at 1600°C.

B. Experimental Procedure

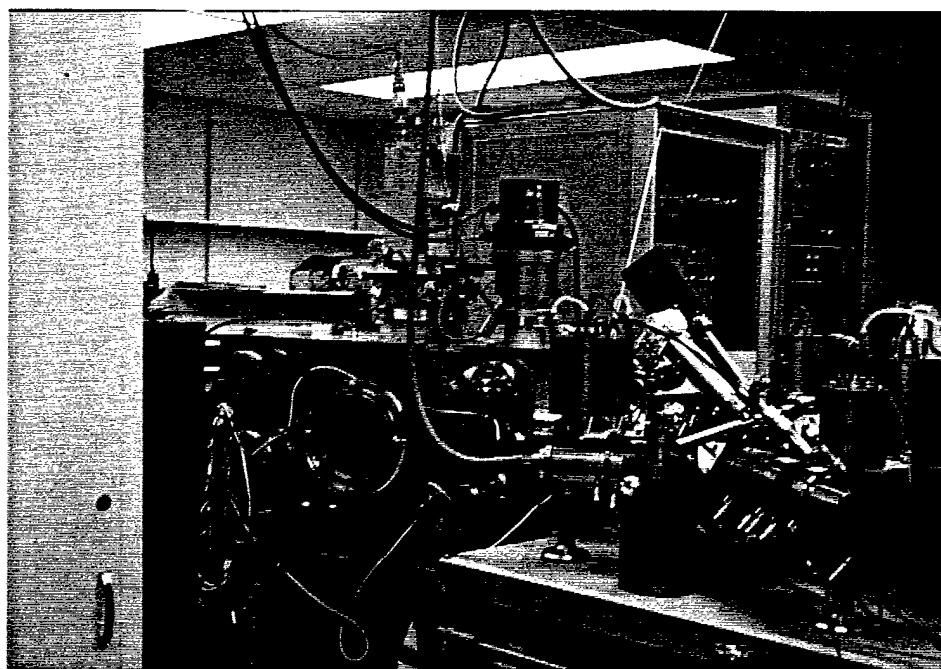
The SSJ was connected to the LEEM as shown in Fig. 1. Considerable efforts were devoted to minimize the vibrations caused by large mechanical pumps in the SSJ. Alignment of the He supersonic beam seeded with NH₃ was accomplished by nitridation of a Si(111) surface at ~1000°C. With an operating pressure of 3×10^{-8} Torr in the LEEM when the beam was directed to the Si surface, the LEED pattern of Si-(7×7) was converted to SiN-(8×8) in a few seconds. However, the LEEM image showed that it took about 2 minutes to complete a full nitride layer, i.e. ~0.5ML/min. Pitot measurements of NH₃ flux gave 1×10^{14} cm²/s which translates into ~5ML/min. on a Si surface. This suggests only 1 out of 10 NH₃ striking the Si(111) surface reacts with Si to form SiN. Great care was taken to maintain the alignment throughout the entire experimental period with the SSJ.

Initial growth experiments with the NH₃ seeded beam at 0.22 eV were unsuccessful. Increasing the NH₃ energy to 0.40 eV by heating the nozzle at 280°C produced GaN growth which could be observed in the LEEM images and in the LEED patterns. The Ga evaporation rate was between 2 and 3 ML/min., and the 6H-SiC(0001) substrate temperature was between 680 and 720°C. Interpretation of the growth process as observed by LEEM was greatly hampered by the vastly different surface qualities and conditions found on the 6H-SiC(0001) substrates. The surface morphology and structure of the substrates varied from sample to sample, despite the fact that all of them had undergone the same cleaning procedure of hydrogen etching at high temperatures performed by Professor Feenstra's research group at Carnegie Mellon University.

Over 80 hours of video tape were recorded by the LEEM over the entire experimental period.



Front view



Rear View

Figure 1. Seeded beam nozzle connected to the LEEM.

C. Results

6H-SiC(0001) Substrates. The last quarterly report showed a LEEM image of a 6H-SiC(0001) surface etched by hydrogen at 1600°C by Feenstra's group. That particular surface showed a regular array of steps and terraces. Unfortunately, not all 6H-SiC(0001) surfaces exhibit the same surface morphology. One of the best crystals examined by the LEEM showed good and clear step structure but pronounced syntaxy, i.e. intergrowth of various polytypes and interlaced steps as shown in Fig. 2, indicating the presence of many screw dislocations whose core, however, could not be located. Another crystal showed clear $(\sqrt{3} \times \sqrt{3})$ -R30° LEED pattern and step structure in small regions around precipitates, but otherwise consisted mainly of regions without recognizable crystal structure as shown in Fig. 3(a). Yet another crystal displayed large disordered regions (dark contrast) and small ordered regions (bright contrast) as shown in Fig. 3(b). This last surface, which served as a substrate for SSJ deposition, provided the most valuable information will be discussed in the next section. Depending on the electron energy used in the LEEM, the bright ordered region could be shown to contain steps and terraces as in the first frame in Fig. 4. However, under these imaging conditions, the disordered region displayed uniformly gray contrast and the heterogeneous grainy structure in Fig. 3(b) disappeared.

The LEEM and other studies on 6H-SiC(0001) substrates thus far suggest that the uniformity of the SiC surfaces must be brought under control before meaningful and reproducible growth studies can be conducted if indeed SiC crystals become the substrate of choice for GaN deposition. It is planned to conduct an in-house etching program to see if some degree of uniformity can be produced in the surface morphology of 6H-SiC(0001) substrates.

GaN Growth. Frame-captured LEEM images showing GaN growth using the NH₃ seeded beam from the SSJ source are shown in Fig. 4. The growth proceeds as follows: in the well-ordered region, i.e. bright contrast region with steps, the steps broaden with a slight change in contrast as shown in the frame at 7 minutes. The $(\sqrt{3} \times \sqrt{3})$ -R30° LEED pattern of this region decreases in intensity without appreciable change in the substrate spots. In the region which is structureless in the LEEM, i.e. region with uniform gray contrast, LEED only shows a weak (1×1) pattern with no recognizable changes in this initial growth phase. This region will be called the "disordered" region.

With increasing deposition time, weak and diffuse arced diffraction features develop with strong secondary electron background as shown in Fig. 5 (84 min., 19.7 eV). The movement and change of these features with energy and focus (Fig. 5, 84 min., 7.0 eV) indicate that they originate from faceted and azimuthally poorly aligned crystals. Interestingly, the LEED pattern from the well-ordered stepped region has much weaker, more diffuse, and azimuthally more misaligned facet features than those of the disordered region. With further deposition, the

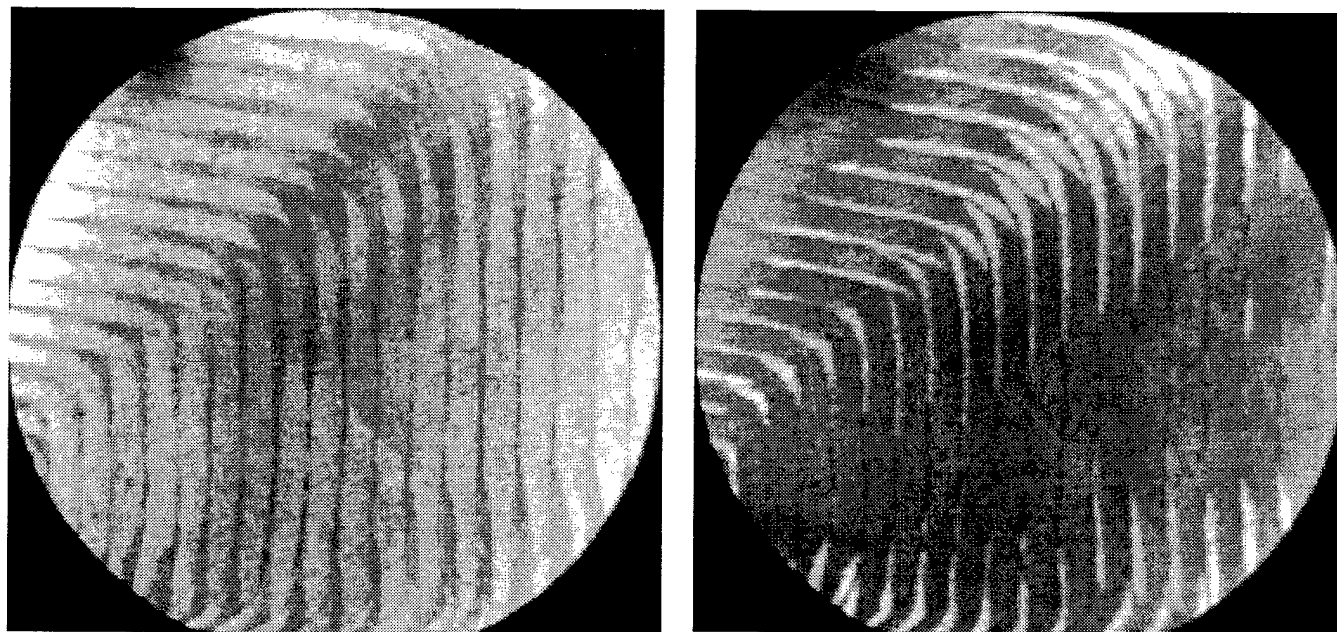


Figure 2. Syntaxy of the 6H-SiC(0001) surface. Different polytypes reverse contrast when electron energy of the LEEM image was changed from 14.1 eV (a) to 15.6 eV (b). Field of view 4.8 μm .

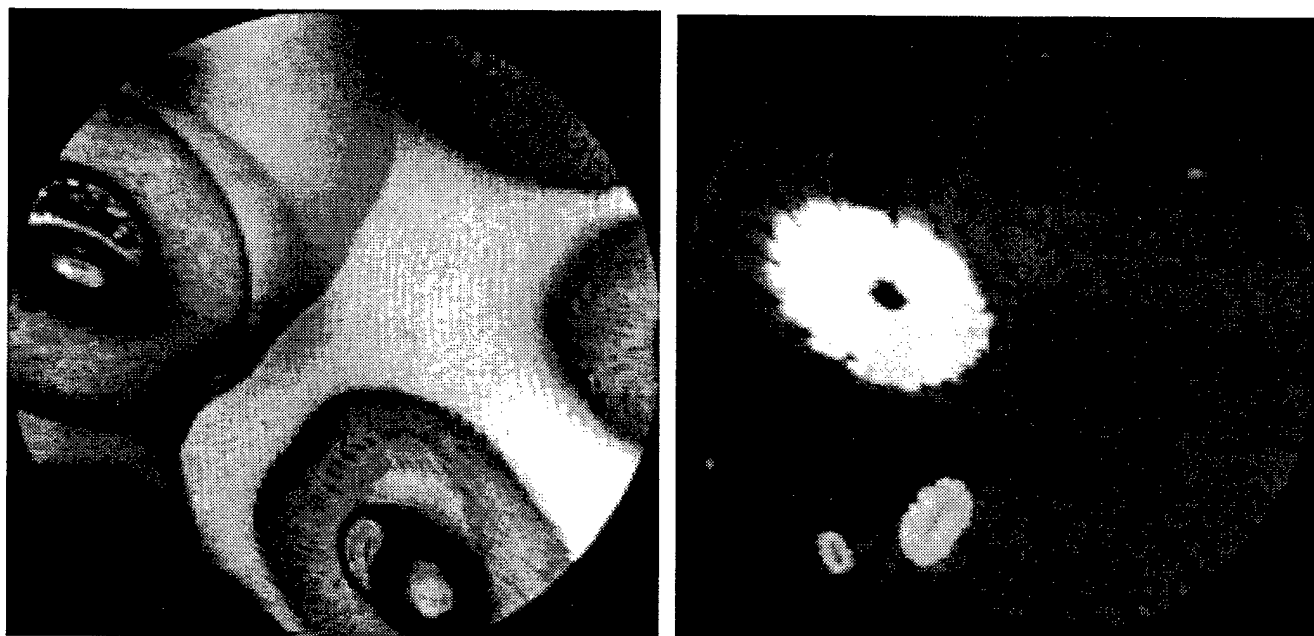
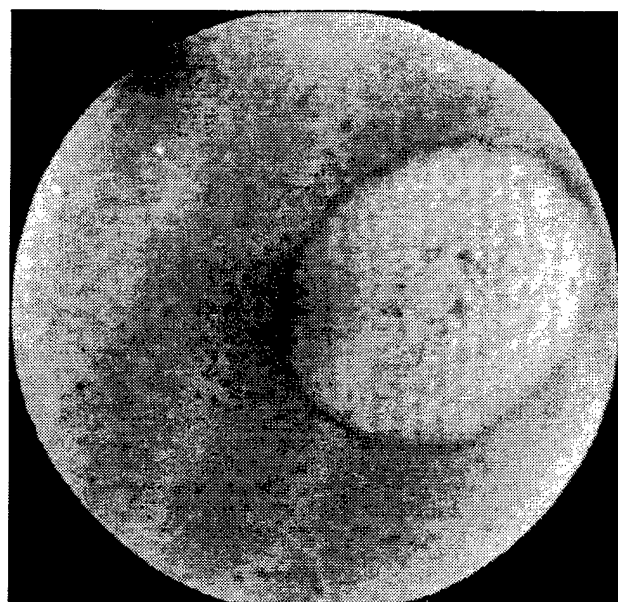
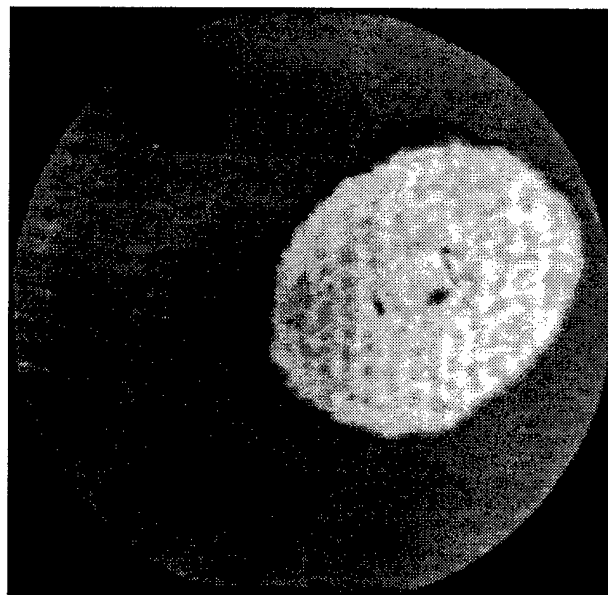


Figure 3. LEEM images showing the heterogeneity of the 6H-SiC(0001) surface in two different crystals. Electron energy is 33.6 eV (a) and 11.0 eV (b). Field of view is 20.6 μm .

diffraction features sharpen, increase in intensity and become less arced (Fig. 5, 145 min). In the LEEM, graininess developed in the ordered region as well as in the disordered region with the appearance of some small bright spots (Fig. 4, 64 min). Finally, when growth is extended to 200 minutes and beyond, the LEEM image in Fig. 4 shows very grainy features in the



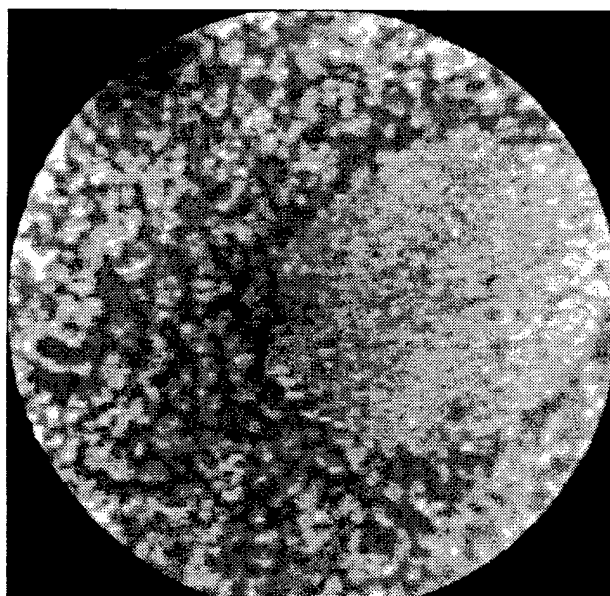
Initial surface



7 min.

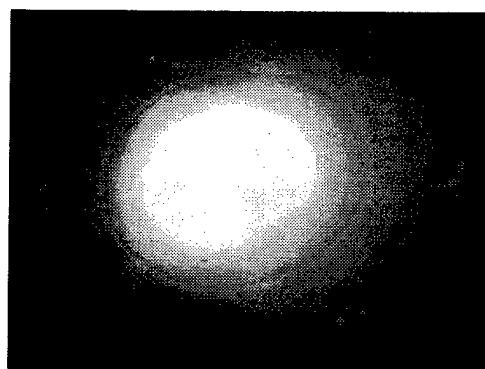


64 min.

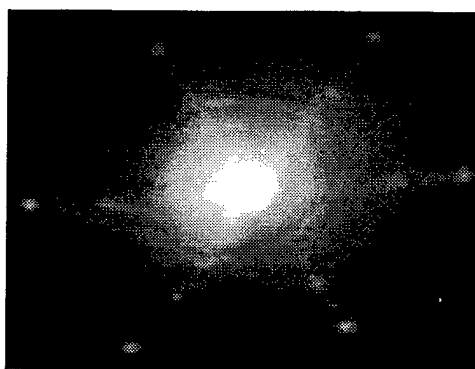


200 min.

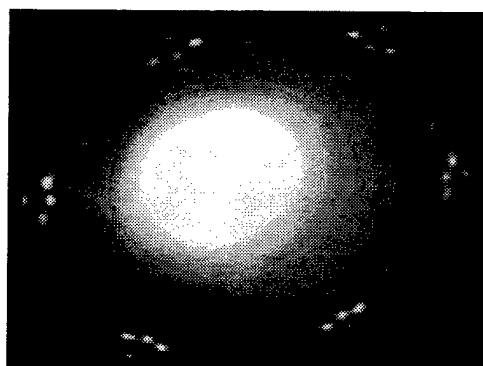
Figure 4. LEEM images of GaN during growth with seeded beam. Time elapsed during deposition is indicated in minutes. Electron energy is 7.0 eV. Field of view is 4.8 μm .



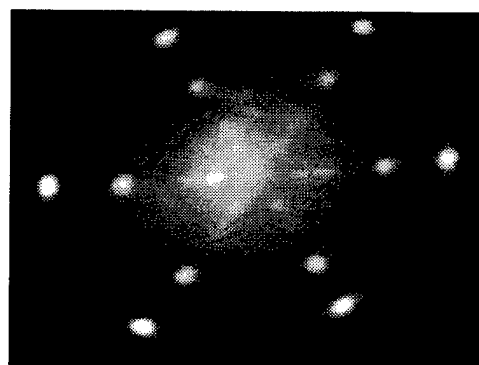
84 min, 19.7 eV



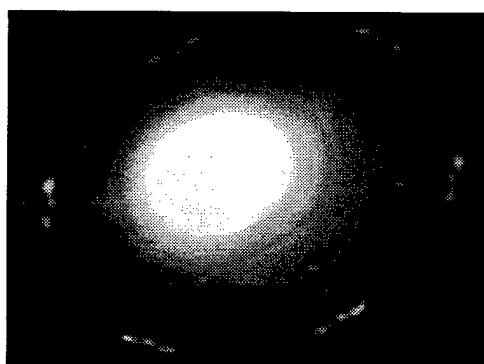
84 min, 7.0 eV



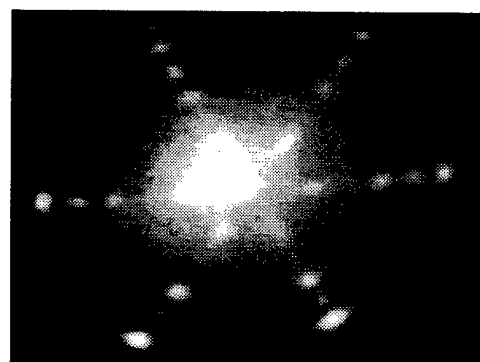
145 min, 19.7 eV



145 min, 7.0 eV



230 min, 19.7 eV



230 min, 7.0 eV

Figure 5. LEED patterns during GaN growth using seeded beam.

originally well-ordered region and aggregates of crystals in the disordered region. The LEED pattern (Fig. 5, 230 min.) continues to sharpen with arcs still visible at 19.7 eV and the spots due to facets intensified at 7.0 eV.

Both the LEEM and LEED results confirm the growth of faceted GaN crystals. A preliminary analysis of LEED shows that growth of the (0001) surface is almost absent with

the dominant facets being $\{10\bar{1}1\}$ and possibly also $\{10\bar{1}2\}$. The growth on the well-ordered region is similar to that reported in the last quarterly report where deposition was conducted with an N-atom RF plasma source. The surface of the grown film is rough on a submicron scale and not bounded by the (0001) plane. Adsorption of oxygen could be a cause for the faceting behavior, but further experiments with gases introduced via a purifier are needed to confirm this conjecture. Gas analysis shows that the $O_2:N_2$ ratio in the NH_3 seeded beam experiments is $\sim 5 \times 10^{-6}$ in the LEEM sample chamber. In the RF plasma source experiments, this ratio is higher and is $\sim 2 \times 10^{-5}$. Post mortem Auger depth profiling shows an oxygen signal throughout the grown film, which could be attributed to oxygen on the side faces of the columnar shaped crystals.

D. Conclusions

The following preliminary conclusions are reached for the results obtained during this quarterly period. More experiments under better defined conditions, especially in regard to the substrates, are obviously needed to provide more definitive conclusions.

Deposition of GaN and AlN by SSJ or by RF plasma source on non-perfect 6H-SiC(0001) substrates do not result in epitaxial growth, but rather forms initially an amorphous or extremely fine-grain crystalline layer. Out of this initial layer, a (0001) growth orientation develops with azimuthally partially aligned small faceted crystals. The azimuthal alignment is achieved either by recrystallization of the initial layer in the ordering field of the substrate or by preferred growth of crystals with favorable alignment with respect to the substrate. Post mortem cross-sectional TEM images of a AlN/SiC interface such as that shown in the previous quarterly report suggests that the reorganization process with its resulting layer replaces the initial disordered surface. The preferred growth of the most favorably oriented crystals eventually leads to increasing perfection of the orientation giving the impression of epitaxy in most of the post mortem studies.

The fact that Group III nitride epilayers have been grown and reported is probably a consequence of the buffer layer. The buffer layer is deposited at low temperature and is very fine grained and sometimes even amorphous. Upon subsequent annealing, the buffer layer recrystallizes epitaxially via solid state epitaxy and this provides a clean and well-ordered template for further growth, a necessary condition for direct epitaxial growth from vapor phase. Thus, it appears that it is not the purity nor the misfit of the substrate surface that determines the quality of the final grown layer. Only the perfection of the buffer layer matters. This explains why good nitride layers can be grown on sapphire which has a large misfit and also on SiC surfaces which contain large regions of disorder.

Future work will be directed to experiments with better defined 6H-SiC(0001) substrates, with well-defined buffer layers, and on other suitable surfaces with sixfold symmetry such as Si(111) with suitable nitridation treatment as described in the previous report.

E. Publication

V. M. Torres, M. Stevens, J. L. Edwards, D. J. Smith, R. B. Doak and I. S. T. Tsong, "Growth of AlN and GaN on 6H-SiC(0001) using a He supersonic beam seeded with NH_3 " Appl. Phys. Lett. (in press).

IV. Selected Energy Epitaxial Deposition (SEED) of III-V Nitride and SiC Thin Films

A. Introduction

Gallium nitride is a wide band gap semiconductor ($E_g=3.4$ eV) with many potential optoelectronics and high-temperature, high-frequency, microelectronics applications. Gallium nitride forms a continuous range of solid solutions with AlN (6.28 eV) and InN (1.95 eV), permitting the fabrication, via band gap engineering, of laser diodes with tunable emission frequencies from covering the visible and UV regions. State-of-the-art GaN films ($\leq 10^8$ defects per cm^2) have been used to fabricate blue light emitting diodes (LEDs) and laser diodes.

Heteroepitaxial growth of high-quality monocrystalline GaN films has been problematic due to the lack of a suitable lattice-matched substrate and the thermodynamic instability of GaN under high-temperature growth conditions. Sapphire, the most common substrate, exhibits a 14% lattice mismatch at the GaN(0001)/sapphire(0001) interface; moreover, the thermal expansion coefficient of sapphire is 25% greater than that of GaN. Only by employing a low-temperature AlN or GaN buffer layer can one obtain monocrystalline GaN films on sapphire with defect densities in the 10^8 – 10^9 cm^{-2} range.

Substrate temperatures in excess of 1000°C are employed for growth of monocrystalline GaN films by halide or metal-organic CVD (MOCVD) using NH_3 . In MOCVD, substrate thermal energy is used to overcome activation barriers for precursor decomposition and adatom surface migration (lateral diffusion); however, GaN decomposition above 620°C *in vacuo* necessitates the use of large V/III flux ratios [1]. Plasma-assisted processes have been utilized to lower the GaN growth temperature to approximately 700°C , but ion-induced damage and oxygen contamination are often observed.

The use of energetic neutral beams of precursor molecules is an alternative approach to the epitaxial growth of GaN films at lower substrate temperatures. In selected energy epitaxy (SEE), heavy reactant molecules are seeded in a supersonic expansion of light molecules and thereby accelerated to hyperthermal energies. The precursor molecules attain kinetic energies on the order of 1-2 eV which can provide the necessary energy for activated surface processes, such as dissociative chemisorption and adatom migration. Hence, in prospect, monocrystalline GaN films may be grown at lower substrate temperatures by SEE than by conventional MOCVD [2]. Moreover, energetic neutral beams with narrow energy distributions are ideal tools for fundamental studies of wide bandgap semiconductor growth using *in situ* low-energy electron microscopy (LEEM) and other techniques.

To demonstrate the potential advantages of SEE, homoepitaxial growth of GaN was investigated obviating the substrate lattice-mismatch issue and allowing us to better isolate the effects of precursor kinetic energy on growth kinetics and film morphology. Preliminary

results of GaN homoepitaxial growth using TEG-seeded and NH₃-seeded supersonic molecular beams were described in the previous report (Mar. 1997). In this report, detailed results of GaN homoepitaxial growth using seeded supersonic beams are presented that elucidate the effects of substrate temperature, NH₃ flux, and Ga flux on growth rate and film morphology. This report also includes preliminary results of GaN growth using a Ga effusion cell and a NH₃-seeded supersonic molecular beam.

B. Experimental Procedure

SEED/XPS Deposition System. The SEED/XPS multi-chamber system described in previous reports (Jun. 1996, Dec. 1996) was used for homoepitaxial growth of GaN. The orifices used in the TEG and NH₃ nozzles were 50 and 150 mm, respectively. Conical skimmers used for extracting both TEG and NH₃ beams from supersonic free jets have an opening of 1 mm in diameter, a base of 20 mm in diameter, an included angle of 25° at the opening and of 70° at the base, and a height of 17 mm. The collimation apertures of 5×5 mm² are located downstream between the 2nd differential pumping stage and the growth chamber. The two molecular beams are directed to the substrate with incident angles of 6° with respect to the surface normal. The deposition area on the vertical substrate is 15×15 mm².

Substrate Preparation/Cleaning. The substrates were 2-μm thick GaN films grown by MOCVD on on-axis 6H-SiC employing a 0.1-μm thick AlN buffer layer. The substrates were provided by M. Bremser and O. Nam of Prof. Davis's group and used as received. Ag paste was used to provide good thermal contact between the Mo sample holder and the GaN/AlN/6H-SiC substrate; two Mo pins were used to hold the substrate in place. The Mo holder was placed on a hot plate to dry the Ag paste for 5 min at 80°C. Subsequently, it was introduced via the load-lock chamber and transferred into the growth chamber *in vacuo*. The load-lock chamber is evacuated by an Alcatel Drytel pump while the transfer lines are evacuated by a APD cryopump. The sample was heated slowly to 400°C under an NH₃ flux for outgassing. Prior to the growth, the GaN substrate was cleaned *in situ* by NH₃ beam exposure at 800°C for 15 min. After *in situ* cleaning, the substrate temperature was lowered to 600 to 750°C under an NH₃ flux.

Homoepitaxial Growth Using Dual Supersonic Beams. Gallium nitride growth was initiated by directing a TEG-seeded supersonic beam to the substrate. Growth runs lasted for 6 h, unless otherwise noted. Gallium nitride films were grown using various ammonia flow rates, TEG bubbler temperatures, and substrate temperatures. The NH₃ nozzle was heated to 200°C, and the stagnation pressure was in the 910-925 Torr range for typical experiments, which employed a NH₃ flow rate of 60 sccm, and a He flow rate of 200 sccm. The He flow rate through the TEG bubbler was held constant at 60 sccm, and the TEG nozzle stagnation

pressure was in the 825-865 Torr range for all growth experiments. Growth rates were determined using a profilometer from the step created by the pins holding the substrate.

Homoepitaxial Growth Using Supersonic NH₃ Beam and Ga Effusion Cell. A hot-lip Ga Knudsen cell (K-cell) manufactured by SVT Associates, Model SVTA-450-20HL, was installed in the growth chamber. The K-cell is equipped with a 20-cc PBN crucible, a water-cooled shroud, integral shutter and a secondary filament which maintains a higher temperature near the crucible lip to prevent Ga condensation. The crucible temperature is measured with a Type C (W-Re) thermocouple. The K-cell is mounted on a 4.5 in. flange, and the lip of the crucible is ~5 in. from the substrate. Two films were grown using the Ga cell and a NH₃-seeded supersonic molecular beam. Growth was initiated by opening the K-cell shutter after both the Ga crucible and the substrate were at the desired temperatures. Initial GaN growth experiments were done at 700°C substrate temperature and 900-950°C K-cell temperature.

XPS Analysis. The UHV surface analysis chamber is equipped with a PHI 3057 XPS system comprising a 10-360 spherical capacitor analyzer (SCA), Omni Focus III fixed-aperture lens, 16-element multichannel detector, and 257 DR11 PC interface card. A OHI 1248 dual-anode (Al/Mg) X-ray source is used. The sample is mounted on a tilt stage which is attached to a precision xyz -rotary manipulator (Thermionics). The analysis chamber is pumped by a Perkin-Elmer TNBX ion pump/TSP combination and has a base pressure of 8×10^{-11} Torr. After growth, samples were transferred to the XPS chamber through vacuum transfer lines. XPS spectra were taken with both Mg and Al anodes to isolate N(1s) and O(1s) signal (using Mg anode), or C(1s) and Ga(2p_{3/2}) signal (using Al anode) from other interfering peaks.

RHEED Analysis. *In situ* reflection high-energy electron diffraction (RHEED) measurements were made using a Fisons LEG 110 15-kV electron gun and 100-mm Al-coated phosphor screen. RHEED patterns of the GaN substrate before and after the *in situ* cleaning were taken at 15kV.

SEM/AFM Analysis. SEM and AFM measurements were made on selected samples to investigate the morphology of the GaN films. SEM images were obtained using a JEOL 6400FE SEM with a cold field emission. The AFM images were obtained using a Digital Instruments Dimension 300 Scanning Probe Microscope with a Nanoscope IIIa Controller. A silicon tip with a nominal tip radius of curvature of 5-10 nm was used.

C. Results and Discussion

Substrate Preparation. Figure 1 shows the XPS results for *in situ* cleaning of the GaN substrate at 800°C and 850°C with and without NH₃-beam exposure. One substrate was heated first at 850°C under NH₃ and then heated at 850°C *in vacuo*. A second substrate was heated first at 800°C *in vacuo*, and then heated at 800°C under an NH₃ flux. The carbon content

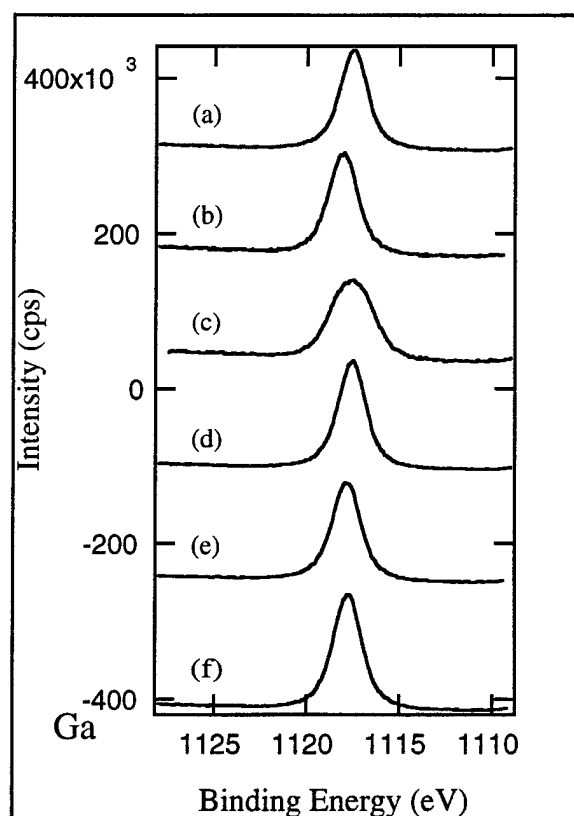
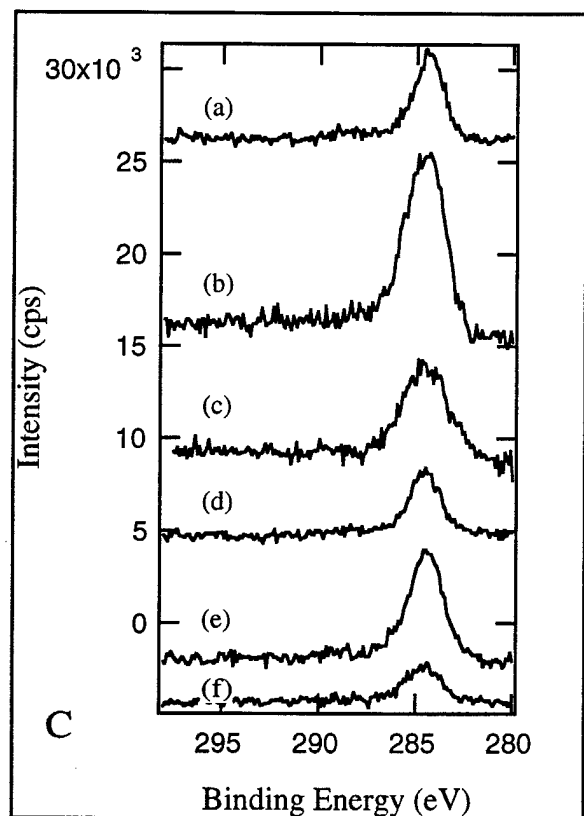
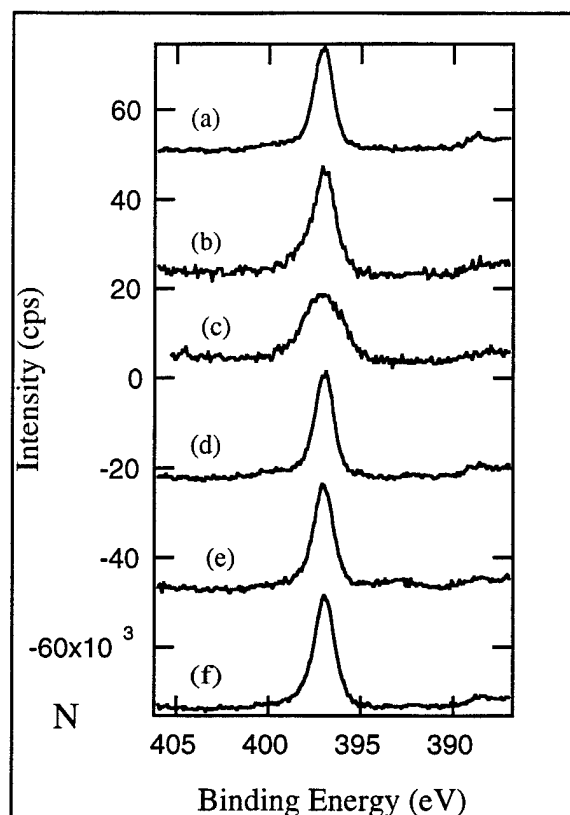
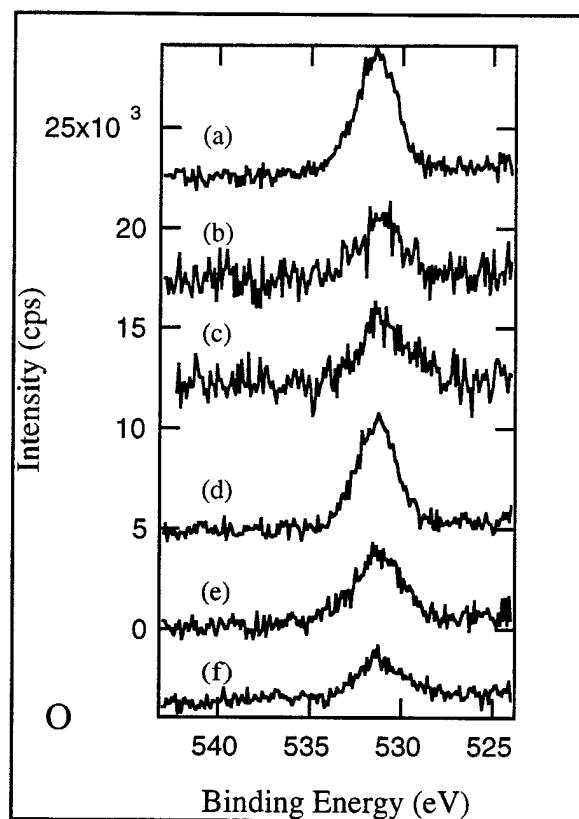


Figure 1. From top to bottom (a-f): a) GaN substrate without cleaning, b) ammonia treatment at 850°C for 15 mins., c) heating at 850°C for 15 mins., d) GaN substrate without cleaning, e) heating at 800°C for 15 mins., f) ammonia treatment at 800°C for 15 mins. Note: a-c, d-f are taken from the same substrate.

increased first and then decreased at each temperature, which suggests that the carbon contamination was from the Ag paste. At each temperature, it is evident that the surface oxygen and carbon concentrations are reduced by heating under an NH₃ flux. The NH₃ flux also stabilized the GaN substrate from decomposition at 850°C [3]. The Ga and N peaks are seen to broaden after heating to 850°C *in vacuo*. Carbon and oxygen concentrations were lower after NH₃ beam cleaning at 800°C than after cleaning at 850°C; however, more than 7 at% of carbon remained. No RHEED pattern was observed before *in situ* cleaning, but RHEED streaks and Kikuchi lines were seen after *in situ* cleaning under NH₃ at 800°C, indicating that a smooth, clean surface was obtained.

Homoepitaxial Growth Using Dual Supersonic Beams. The growth rate and XPS-derived Ga/N stoichiometry for GaN films grown under various growth conditions are given in Table I.

Table 1. Homoepitaxial Film Growth Conditions, Growth Rates and Stoichiometries

Film	Growth Temperature	NH ₃ Flowrate (sccm)	TEG Bubbler Temperature	Growth Rate (nm/hr)	Ga/N Ratio [†]
1*	700°C	60	0.8°C	18	0.75
2*	700°C	60	10°C	51	0.90
3*	700°C (3 h)	60	20°C	52	1.07
4*	700°C	40	10°C	31	0.88
5	700°C	20	10°C	21	0.96
6*	750°C (3 h)	60	20°C	35	1.38
7*	650°C	60	10°C	37	1.07
8*	600°C	60	10°C	37	1.07

* Films imaged using SEM.

[†] Determined by XPS.

The GaN growth rate at 700°C increased markedly when the TEG bubbler temperature was increased from 0.8 to 20°C, approximately doubling the Ga flux. In contrast, the GaN growth rate remained almost the same when the TEG bubbler temperature was raised from 10°C to 20°C, doubling the Ga flux again. It is noted that the Ga/N ratio is > 1.0 for Film 3, indicating a Ga-rich growth surface. These results suggest that growth is NH₃-limited at 700°C and 60 sccm NH₃ for TEG bubbler temperatures ≥ 10°C. A decrease in the NH₃ flux resulted in a decrease in the growth rate at 700°C (Films 3, 4 and 5) confirming that these films were grown under NH₃-limiting conditions [4]. The maximum growth rate was obtained when the growth temperature was at 700°C. GaN growth at 600°C and 650°C occurred at equivalent rates of 37 nm/h, and GaN growth at 750°C was only observed when the TEG bubbler temperature

was 20°C, suggesting that a larger Ga flux was needed at 750°C owing to greater Ga re-evaporation. The surface carbon concentration ranged from 18% to 22% for films deposited using TEG-seeded beams at 700°C. Preliminary results indicate a reduction in carbon contamination with increasing TEG flux. The Ga and N XPS peaks are broader for the epilayers than for the substrate indicating a wider range of a chemical bonding environments.

Film Morphology. SEM and AFM images of the GaN films grown using dual seeded supersonic beams show the films to have rough, highly faceted surfaces with the GaN growing in pyramidal islands. Figure 2 shows the SEM image of a film grown at 700°C with 60 sccm NH₃ and TEG bubbler temperature of 10°C (Film 2). The image is representative of the typical film morphology. More defined pyramidal shapes and lower surface coverage are seen for films grown at higher temperatures. Figure 3 shows that at lower growth temperatures the islands are more rounded illustrating that as the growth temperature is increased, surface diffusion rates are sufficient to allow the islands to acquire equilibrium shapes. At lower growth temperatures, there is less Ga re-evaporation, and the higher surface Ga content results in a smoother film. This effect is also seen by increasing the Ga flux for films grown at 700°C, as is evident by comparing Figs. 4 and 5. (Note: The cracks seen in these films are a result of the high Si doping of the GaN substrate and not a result of the growth conditions.) The RMS roughness measured using AFM indicates the same trend: by doubling the Ga flux the RMS roughness decreased from 53 to 21 nm. The films with surface Ga/N stoichiometries close to ideal (Runs 8 and 3) had the smoothest morphologies.

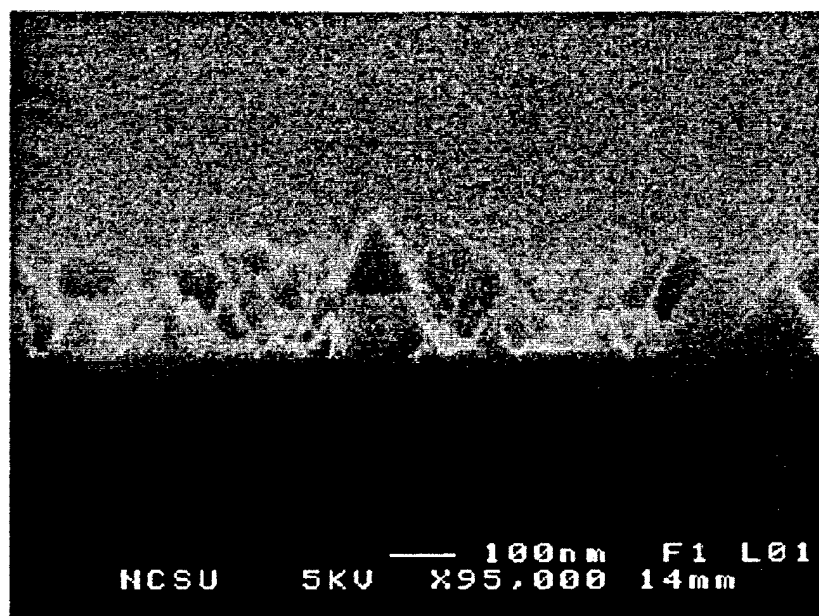


Figure 2. GaN grown 700°C, 60 sccm NH₃ and 10°C TEG.

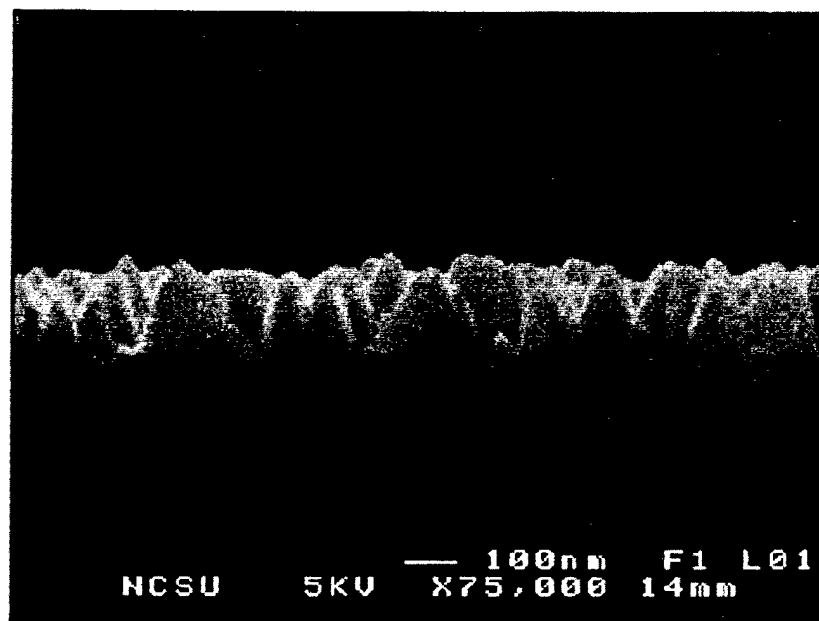


Figure 3. GaN grown 600°C, 60 sccm NH_3 and 10°C TEG.

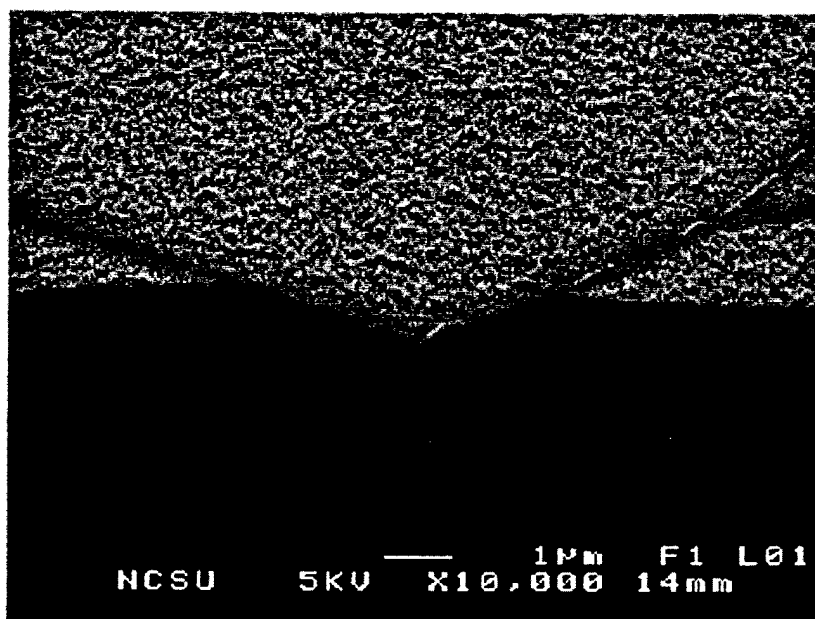


Figure 4. GaN grown 700°C, 60 sccm NH_3 and 10°C TEG.

Homoepitaxial Growth Using Supersonic NH_3 beam and Ga K-cell. Two runs were done at Ga K-cell temperatures of 906°C and 950°C. The substrate position in the run at 950°C was 1" forward, closer to the Ga K-cell, than in the run at 906°C. In the latter case, the substrate was located at the position used for growth with dual supersonic molecular beams. The growth

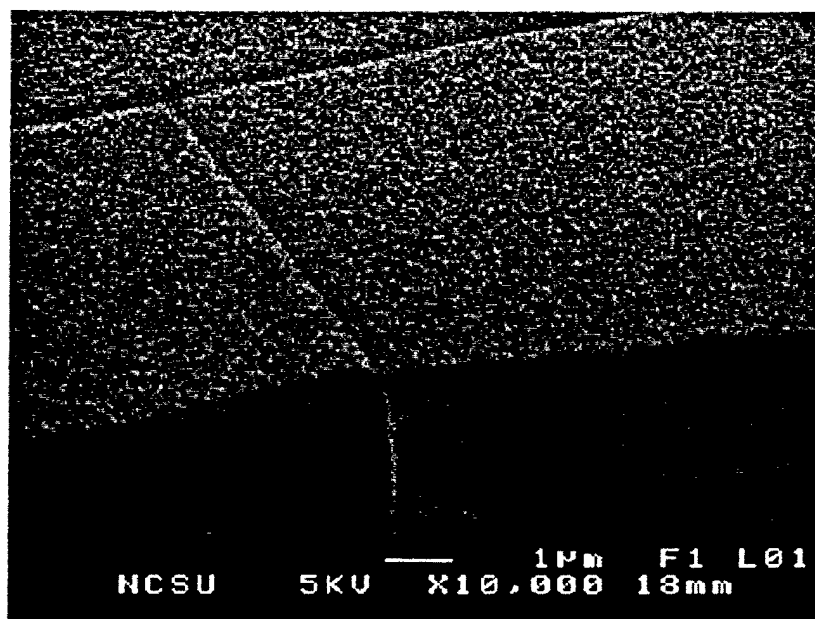


Figure 5. GaN grown 700°C, 60 sccm NH₃ and 20°C TEG.

rate for the run at 906°C K-cell temperature was 37 nm/hr, and the growth rate for the run at 950°C was 130 nm/hr, which is significantly higher than the growth rates achieved using a TEG-seeded supersonic beam. The surface carbon concentration of films grown using the Ga K-cell are significantly lower than those of TEG-derived films (Table II). This result indicates that some of the carbon contamination was contributed by the metal-organic Ga source. The surface oxygen concentrations are equivalent.

Table II. Surface Carbon and Oxygen Concentrations of Films Grown by Using TEG Supersonic Beam and Ga K-cell.

Ga source	Carbon percentage	Oxygen percentage
TEG supersonic beam	18-22%	5-10%
Ga cell at 906°C	10%	8%
Ga cell at 950°C	14%	7%

Note: All these runs were at 700°C growth temperature and 60 sccm NH₃.

D. Conclusions

Homoepitaxial growth of GaN using TEG- and NH₃-seeded supersonic beams was achieved, and the films were characterized by XPS, RHEED, SEM and AFM. The GaN films

exhibit a highly faceted surface morphology, but have smoother surfaces as the Ga flux is increased.

E. Future Plans

A more detailed investigation of GaN homoepitaxial growth will be done to reveal the relationship between film quality and molecular kinetic energies tuned by supersonic beams.

Growth of GaN will be monitored *in situ*, using RHEED in order to relate growth patterns to molecular kinetic energies.

Time of flight (TOF) measurements will be taken in order to find out the velocity and kinetic energy distribution of the supersonic molecular beams.

A new gas line for generating TEA (triethylaluminum) supersonic beam will be installed to grow an AlN buffer layer on sapphire and 6H-SiC substrates.

A radio-frequency discharge nozzle/nitrogen atom source will be constructed and installed in the system. This source will produce a supersonic beam of atomic nitrogen and will be used in conjunction with the TEG supersonic source as well as the Ga effusion cell. The atomic nitrogen source will be used to compare the efficiencies of atomic nitrogen to ammonia in the GaN growth. The design will follow those of Pollard and Mullins [5,6].

A detailed comparison of results using Ga effusive and TEG supersonic molecular beams will be made.

F. References

1. S. Nakamura, Japan. J. Appl. Phys. **30**, L1705(1991).
2. M. R. Lorenz and B. B. Binkowski, J. Electrochem Soc. **109**, 24(1962).
3. Z.A. Munir and A. W. Searcy, J. Chem. Phys. **42**, 4223(1965).
4. R. Held, D. E. Crawford, A. M. Johnston, A. M. Dabiran and P. I. Cohen, J. Electron. Mater. **26**, 272(1997).
5. C. B. Mullins, Appl. Phys. Lett. **68**, 3314 (1996).
6. J. E. Pollard, Rev. Sci. Instrum. **63**, 1771 (1992).

V. Dual Colutron Ion-Beam Deposition

Previous reports have discussed monoenergetic and mass separated ion beams of N_2^+ , N^+ and Ga^+ at ~ 20 eV with FWHM of ~ 1 eV. During the current report period, nitridation experiments have been conducted on Si(100) wafers with the N_2^+ and N^+ ion beams. Fig. 1 shows the SIMS depth profiles of (top) a clean Si(100) wafer, (middle) a Si(100) surface nitrided with N_2^+ ions, and (bottom) a Si(100) surface nitrided with N^+ ions.

The energy of the N_2^+ ion beam was 38 eV with a FWHM of 3 eV and the current was ~ 40 nA. This means a full nitride layer would take about 45 minutes to complete. The nitridation time for the N_2^+ beam was 18.5 hours.

The energy of the N^+ ion beam was 40 eV with a FWHM of 2 eV and the current was ~ 8 nA. A full nitride layer would take almost 4 hours to complete at this low ion current. The nitridation time for the N^+ beam was 20 hours.

Compared with the top SIMS depth profile of the clean Si(100) surface where the nitrogen signal, represented by CsN^+/Cs^+ , drops very rapidly to zero (10^{-4} on the count scale is essentially zero), both the surfaces nitrided with N_2^+ and N^+ clearly show slowly decaying nitrogen signal in Fig. 1. Because of the low energies of the N_2^+ and N^+ ions, the depth profiles are not due to implanted nitrogen, but due to formation of SiN layers. The depth profile for N_2^+ nitridation extends deeper than that for N^+ nitridation because N_2^+ ion current was 5 times larger. However, the N_2^+ nitrided layer was obviously not 5 times thicker than the N^+ nitrided layer because N^+ was far more reactive than N_2^+ which needs to dissociate before reacting with Si.

In summary, work has demonstrated that the Colutron dual ion-beam system can be used to perform nitridation of the Si(100) surface with low-energy, nearly monoenergetic, and mass separated N_2^+ and N^+ ion beams. Work is underway to deposit GaN layers by Ga^+ and N_2^+ (or N^+) beams.

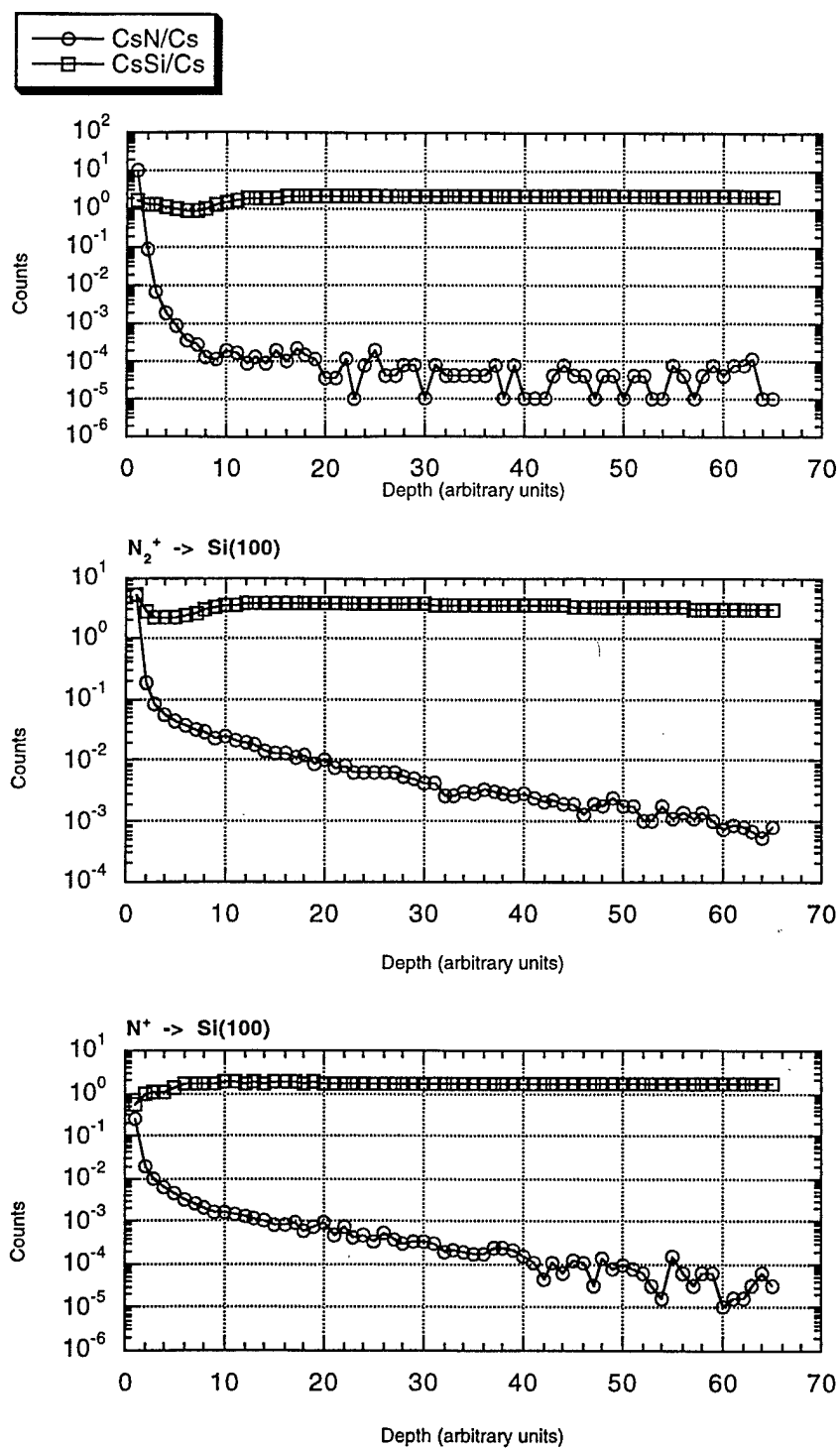


Figure 1. SIMS depth profiles of (top) a clean Si(100) wafer, (middle) a Si(100) surface nitrided with N_2^+ ions, and (bottom) a Si(100) surface nitrided with N^+ ions

VI. Distribution List

Dr. Colin Wood Office of Naval Research Electronics Division, Code: 312 Ballston Tower One 800 N. Quincy Street Arlington, VA 22217-5660	3
Administrative Contracting Officer Office of Naval Research Regional Office Atlanta 100 Alabama Street, Suite 4R15 Atlanta, GA 30303	1
Director, Naval Research Laboratory ATTN: Code 2627 Washington, DC 20375	1
Defense Technical Information Center 8725 John J. Kingman Road, Suite 0944 Ft. Belvoir, VA 22060-6218	2